Raman and infrared spectroscopic study of the borate mineral kaliborite

Andrés López[a], Ricardo Scholz,[b] Ray L. Frost[a•]

[a] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[b] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG, 35,400-00, Brazil

Abstract

We have studied the mineral Kaliborite. The sample originated from the Inder B deposit, Atyrau Province, Kazakhstan and is part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil. The mineral is characterized by a single intense Raman band at 756 cm^{-1} assigned to the symmetric stretching modes of trigonal boron. Raman bands at 1229 and 1309 cm^{-1} are assigned to hydroxyl in-plane bending modes of boron hydroxyl units. Raman bands are resolved at 2929, 3041, 3133, 3172, 3202, 3245, 3336, 3398 and 3517cm^{-1}. These Raman bands are assigned to water stretching vibrations. A very intense sharp Raman band at 3597 cm^{-1} with a shoulder band at 3590 cm^{-1} is assigned to the stretching vibration of the hydroxyl units. The Raman data are complimented with infrared data and compared with the spectrum of kaliborite downloaded from the Arizona State University data base. Differences are noted between the spectrum obtained in this work and that from the Arizona State University data base. This research

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)
P +61 7 3138 2407 F: +61 7 3138 1804

shows that minerals stored in a museum mineral collection age with time. Vibrational spectroscopy enhances our knowledge of the molecular structure of kaliborite.

Key words: kaliborite, borate, hydroxyl, Infrared, Raman spectroscopy

Introduction

The mineral kaliborite [1] is a borate mineral of formula $KHMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$ found in potash marine deposits. The mineral was first described from Schmidtmannshall, Aschersleben, Stassfurt Potash deposit, Saxony-Anhalt, Germany **[2]**. Other important occurrences were also reported in the salt deposits at Sambuco mine, Calascibetta Sicily [1]; at the Inder Lake deposits, Kazakhstan [3] and at Doğanlar boreholes Emet, Kütahya Province, Turkey [4]. The mineral is monoclinic of Point Group 2/m with *Space Group: C2/c*. a = 18.572(6)Å b = 8.466(3)Å, c = 14.689(5)Å with z=4 [5, 6]. Burns and Hawthorne [1] solved the structure of kaliborite. Kaliborite is one of two borate minerals that are known to contain a crystallographic symmetric hydrogen bond.

There have been a number of studies of the infrared spectra of borates as both solids and in solution [7-10]. No infrared studies of kaliborite have been forthcoming. No Raman studies of this mineral have been reported. A number of thermal analysis studies have been undertaken on kaliborite [11-13]. The authors have undertaken a number of vibrational spectroscopic studies on borate minerals [14-23]. In this work we extend our studies to that of the borate mineral kaliborite. As part of our comprehensive research into minerals containing oxyanions, we report the vibrational spectroscopy of kaliborite and relate the spectra to the structure of the mineral.

Experimental

Samples description and preparation

The kaliborite sample studied in this work is from the Inder B deposit, Atyrau Province, Kazkhstan.The sample is part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-140. Kaliborite

sample was gently crushed and the associated minerals were removed under a stereomicroscope Zeiss Stemi DV4 from the Museu de Ciência e Técnica of the Federal University of Ouro Preto.

Raman microprobe spectroscopy

Crystals of kaliborite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

An image of the kaliborite crystals measured is shown in the graphical abstract. Clearly the crystals of kaliborite are readily observed, making the Raman spectroscopic measurements readily obtainable. A spectrum of kaliborite which was downloaded from the RRUFF web site is given in the supplementary information as Figure S1.

Infrared spectroscopy

Infrared spectra of kaliborite were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1}

range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Lorentzian-Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

The Raman spectrum of kaliborite in the 4000 to 100 cm^{-1} spectral range is displayed in Figure 1a. This Raman spectrum shows complexity with a number of overlapping Raman bands. This spectrum shows the position and relative intensities of the Raman bands. It is noted that there are large parts of the spectrum where no intensity or minimal intensity is observed. Thus, the spectrum is subdivided into subsections depending upon the type of vibration being studied.

The infrared spectrum of kaliborite in the 4000 to 500 cm^{-1} spectral region is shown in Figure 1b. This figure shows the position of the infrared bands and their relative intensities. It is noted that there is apparent a large number of overlapping bands. This spectrum displays the position and relative intensities of the infrared bands. As for the Raman spectrum, there are

parts of the spectrum where little or no intensity is observed. Thus, the infrared spectrum is subdivided into sections according to the type of vibrational mode being studied.

The Raman spectrum of kaliborite over the 1400 to 800 cm^{-1} spectral range is reported in Figure 2a. In the Raman spectrum of kaliborite, a single intense band is observed at 756 cm^{-1} with low intensity shoulder bands observed at 775 and 793 cm^{-1}. The Raman band at 756 cm^{-1} is assigned to the symmetric stretching modes of trigonal boron. In the RRUFF spectrum of kaliborite (Figure S1) a Raman band is observed at 757 cm^{-1}, which is in agreement with this work. A series of Raman bands are observed at 847, 881, 944, 967, 1065, 1084, 1144, 1229 and 1309 cm^{-1}. The Raman bands at 847, 881, 944, 967 are assigned to the symmetric stretching modes of trigonal boron [24]. In the RRUFF Raman spectrum of kaliborite, Raman bands are found at 823, 877 and 968 cm^{-1} which is in close harmony with the Raman spectral results reported in this work. It is probable that the Raman bands at 1065, 1084, 1144 cm^{-1} are are due to the antisymmetric stretching modes of tetrahedral boron [24]. In the RRUFF spectrum of kaliborite, Raman bands are noted at 1028 and 1195 cm^{-1}. The two Raman bands at 1229 and 1309 cm^{-1} are assigned to OH in-plane bending modes of BOH [24].

The infrared spectrum of kaliborite over the 1150 to 900 cm^{-1} spectral range is shown in Figure 2b. The infrared spectrum is complex with multiple overlapping bands. The series of infrared bands in this spectral range are assigned to the antisymmetric stretching modes of tetrahedral boron [24] (see Table 11.VIII of this reference). It is expected that the intensity of these bands in the infrared spectrum would show much greater intensity in the infrared spectrum. The infrared bands over the 1000 to 1150 cm^{-1} may be due to BOH bending modes.

The Raman spectrum of kaliborite over the 800 to 300 cm^{-1} spectral range is reported in Figure 3a. The use of the diamond ATR cell for infrared spectroscopy has a lower wavenumber limit of around 550 cm^{-1}, and as a consequence no infrared data for this region were not obtained. One of the strong advantages of Raman spectroscopy is the ability to obtain spectral data below 400 cm^{-1}. A significant number of Raman bands is observed in this spectral region. Intense Raman bands are found at 551 and 639 cm^{-1}. These bands are assigned to the bending modes of trigonal and tetrahedral boron. In the RRUFF spectrum of kaliborite, Raman bands are noted at 589 and 663 cm^{-1}. The most intense Raman band in the RRUFF spectrum is found at 414 cm^{-1} with shoulder bands at 392 and 430 cm^{-1}. It is suspected that the other low intensity bands at 519, 526, 567, 609 and 670 cm^{-1} are also assigned to to the bending modes of trigonal and tetrahedral boron.. There appears to be more Raman bands in ourt spectrum compared with that of the RRUFF spectrum. The kaliborite sample from the museum is more than 100 years old. It is possible that the kaliborite smple has deteriorated and other borite minerals have resulted.

The Raman spectrum of kaliborite over the 300 to 100 cm^{-1} spectral range is reported in Figure 3b. Raman bands of considerable intensity are observed. Raman bands are found at 121, 151, 177, 184, 197, 218, 242, 259 and 320 cm^{-1}. The Raman band at 320 cm^{-1} maybe due to a metal oxygen vibration. Other Raman bands in this spectral region are simply attributed to external vibrations of the lattice. In the RRUFF spectrum of kaliborite, Raman bands are found at 143, 161, 230 and 260 cm^{-1}. There does not appear to be any correspondence between the spectrum reported here in this spectral region and that of the RRUFF spectrum.

The Raman spectrum of kaliborite over the 3800 to 2500 cm^{-1} spectral range is shown in Figure 4a. The spectral profile is broad with a series of overlapping bands noted. Raman bands are resolved at 2929, 3041, 3133, 3172, 3202, 3245, 3336, 3398 and 3517cm^{-1}. These

Raman bands are assigned to water stretching vibrations. A very intense sharp Raman band at 3597 cm^{-1} with a shoulder band at 3590 cm^{-1} is assigned to the stretching vibration of the OH units. The infrared spectrum of kaliborite over the 3600 to 2500 cm^{-1} spectral range is shown in Figure 4b. The spectrum appears broad and complex with a significant number of bands. Infrared bands are noted at 2779, 2916, 3061, 3128, 3188, 3215, 3280, 3329, 3288, 3442 and 3530$cm^{-1}cm^{-1}$. These bands are attributed to water stretching vibrations. The infrared band at 3595 cm^{-1} with a shoulder at 3584 cm^{-1} is due to the stretching mode of the hydroxyl units. Both the Raman and infrared spectra show that water is involved in the structure of kaliborite in different molecular environments. It is noted that the RRUFF spectrum is terminated at 1200 cm^{-1} and no bands above this wavenumber are given. The mineral kaliborite of formula $KHMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$ has 10 OH units and 4 water moieties. The question arises as to whether all the water and OH units are equivalent. XRD data supports the equivalence of the units **[1]**. However, all the units may not be equivalent. Thus resulting in not a single band being observed in the Raman and infrared spectra but rather multiple bands being observed.

The Raman spectrum of kaliborite over the 1800 to 1400 cm^{-1} spectral range is shown in Figure 5a. Raman bands are observed at 1444, 1448 and 1595 cm^{-1}. The band at 1595 cm^{-1} is assigned to the water bending mode. The Raman bands at 1444 and 1448 cm^{-1} is ascribed to the antisymmetric vibrations of trigonal boron [24] (see Table 11.VIII of this reference). The infrared spectrum of kaliborite over the 1700 to 1200 cm^{-1} spectral range is shown in Figure 5b. The infrared spectrum in this spectral region displays infrared bands at 1182, 1276, 1301, 1319, 1350, 1373, 1396, 1428, 1588, 1620 and 1655 cm^{-1}. Weir [10] noted strong infrared bands at 1185 and 1350 cm^{-1}. Valyashko and Vlasova [8] also found broad bands in this spectral region. The infrared band at 1182 cm^{-1} is assigned to the OH in-plane bending mode. The group of infrared bands in the 1250 to 1450 cm^{-1} are assigned to the antisymmetric

178 vibrations of trigonal boron. The infrared bands at 1588, 1620 and 1655 cm^{-1} are attributed to
179 the water bending mode.
180
181 **Conclusions**
182 Borate minerals including kaliborate all contain boron which has a low atomic number, thus
183 making it difficult to determine using EDS techniques. Further, many borate minerals lack
184 crystallinity making measurement by XRD difficult. Vibrational spectroscopy is an ideal
185 methodof characterising borate minerals. What this research shows is that minerals stored in a
186 museum mineral collection age with time and may not provide a unique spectrum of, in this
187 case kaliborate.
188
189 A combination of Raman and infrared spectroscopy has been used to study the borate mineral
190 kaliborite. Bands attributed to the water hydroxyl stretching, bending and librational modes
191 are identified and show the existence of different types of water molecules in the structure,
192 namely weakly and strongly hydrogen-bonded. A number of borate symmetric stretching
193 vibrations are observed and a number of antisymmetric stretching modes are observed
194 consistent with a loss of symmetry of the borate anion in the mineral crystals. The loss of
195 symmetry also results in several in-plane and out of plane bending modes.
196
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